Photodegradation of High Polymers

Part VI - Photolysis of Polystyrene Films in Vacuum and in Air

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June 16, 1965

Previous Reports in This Series

"Part I - The Homogeneous Ionic Polymerization of α-Methylstyrene," R.B. Fox and L. Isaacs, NRL Report 5518, Aug. 19, 1960

"Part II - Vacuum Photolysis of Poly-α-Methylstyrene," Suzanne Stokes and R.B. Fox, NRL Report 5591, Feb. 20, 1961

"Part III - Photolysis of Poly(Methyl Methacrylate) in Vacuum and in Air," R.B. Fox, L.G. Isaacs, Suzanne Stokes, and L.W. Daasch, NRL Report 5720, Dec. 14, 1961

"Part IV - Photolysis of Poly(Methyl Acrylate) in Vacuum and in Air," R.R. Fox, L.G. Isaacs, Suzanne Stokes, and R.E. Kagarise, NRL Report 5894, Feb..13, 1963

"Part V - Photolysis of Poly(Alkylene Polysulfides) in Vacuum," L.G. Isaacs and R.B. Fox, NRL Report 6202, Feb. 4, 1965

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ABSTRACT

Thin films of polystyrene have been photolyzed by 2537A radiation in vacuum and in air at 25°, 80°, and 120°C. Random scission and crosslinking occur simultaneously, with oxygen acting to inhibit the latter process. In air, the apparent quantum yields for random scission, measured by viscosity changes, are 9×10^{-5} and 7×10^{-4} scissions per quantum absorbed at 25° and 120°C, respectively. Crosslinks exceed scissions in vacuum, and no reduction in viscosity is observed; the ratio of crosslinks to scissions increases with temperature in the 25° to 120°C range. During photolysis, hydrogen appears to be the major volatile product emanating from the polymer itself. Of the remaining volatile products, carbon monoxide, carbon dioxide, and methane probably arise from polymer imperfections; benzene and monomer are present as impurities rather than major photolysis products. Large variations in the product yields, which are very small on an absolute scale, and the detection of ethylene from one batch and acetylene from another emphasize the importance of small impurities and imperfections in the photolysis of a highly stable polymer such as polystyrene. Changes in the ultraviolet spectra during photolysis are compatible with the formation of conjugated double bonds along the main chain; in air, these changes are supplemented by oxidation which results in carbonyl formation along the chain and a relatively small fragment absorbing at about 340 mμ.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

PHOTODEGRADATION OF HIGH POLYMERS

PART VI - PHOTOLYSIS OF POLYSTYRENE FILMS IN VACUUM AND IN AIR

INTRODUCTION

Other reports from this Laboratory have dealt with the photolysis of poly(α-methylstyrene) films (1) and solutions (2), polystyrene solutions (3), poly(methyl methacrylate) films (4), and poly(methyl acrylate) films (5). To complete the series of prototype film studies, an investigation of the photolysis of polystyrene films in air and in vacuum was undertaken.

Much of the literature of polymer photodegradation has been reviewed in our previous reports or has been covered in the reviews of Jellinek (6) and Grassie (7). Polystyrene has been the subject of a number of radiolytic and thermolytic studies. Photolysis of polystyrene has received little attention except from the practical standpoint of oxidative degradation under irradiation by light of wavelengths greater than 3000A (8-12). At these wavelengths, the absorption coefficients of polystyrene are quite small. Consequently, rather lengthy exposures at temperatures of 60°C and higher were required to obtain measurable degradation: quantum yields were not reported. It was found that polystyrene oxidation in the presence of ultraviolet radiation occurs mainly at the carbon atoms to which the phenyl groups are bonded. A postirradiation effect was noted and ascribed in part to photo-isomerization similar to the cis-trans isomerization of benzalacetophenone. Achhammer and co-workers (10) carried out a mass spectrometric examination of the volatile products formed during the ultraviolet (3130A) irradiation of polystyrene in vacuum and in the presence of oxygen at 115° to 120°C. Two general processes were observed: (a) the evolution of volatiles arising from the solvents, impurities, and the decomposition of thermolabile structures, and (b) oxidative degradation which resulted in crosslinking, discoloration, and the formation of low-molecular-weight oxygenated products.

EXPERIMENTAL METHOD

Materials

Spectroscopic-grade or freshly distilled solvents were used throughout this work. Tetrahydrofuran was distilled and stored under nitrogen after treatment with lithium aluminum hydride.

Two samples of polystyrene were used: they were prepared and purified in the same way but differed in the proportion of catalyst used in the preparation. Styrene monomer was washed with 5% aqueous sodium hydroxide, dried, and distilled at 20 torr. A heart cut was taken and 60 ml mixed with 1 g of benzoyl peroxide (this gave the sample designated PS-1; 0.5 g of catalyst was used for PS-2). After thorough degassing, the material was sealed off and heated at 50°C for 3 days. The resulting polymer was precipitated twice from tetrahydrofuran solution with methanol and dried in vacuum at room temperature. About 40 g of polymer was recovered in each run. Samples PS-1 and PS-2 had intrinsic viscosities of 0.458 and 0.662 dl/g, respectively, in benzene at 30°C.

Apparatus

Mass spectrometric analyses were carried out with a modified Consolidated Electro-dynamics Corp. Model 21-103C mass spectrometer. Ultraviolet spectra were measured with a Perkin-Elmer Spectracord Model 4000 recording spectrometer.

Ultraviolet exposures were carried out in a quartz apparatus similar to that described previously (1) and limned in Fig. 1. Also shown in the figure is the radiation source, the housing of which acts as a shield and contains a movable window, and the phototube used as a monitor for the radiation emitted by the source. This assembly has been described in detail elsewhere (13). A Hanovia 93A-1 low-pressure mercury lamp producing pri-marily 2537A radiation as the photolytically active wavelength was used in this work. The distance from source to film was 15 cm, and heating effects from the source were negli-gible. Incident radiation was determined by ferrioxalate actinometry (14); approximately 5×10^{18} quanta/g/min were absorbed by the films used in this work, which was carried
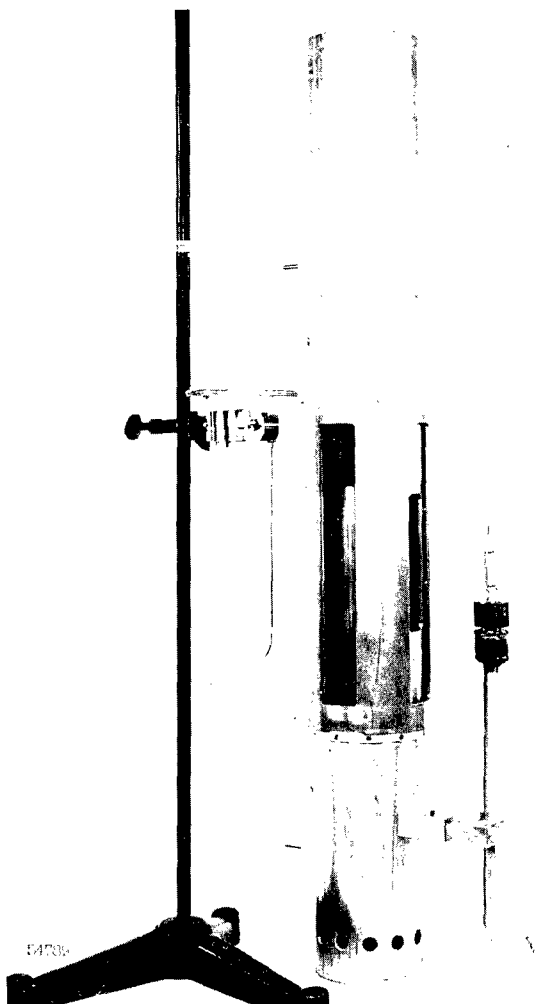

Fig. 1 - Portable radiation shield with ultra-violet source, showing phototube monitor and quartz irradiation chamber

out at constant intensity. For runs above room temperature, the quartz cell was placed in a heating mantle consisting of two concentric brass tubes between which was coiled nichrome heating wire; a window approximately 2×7 in. was cut through the tubes to allow exposures to be made.

A ^{60}Co source was used in the gamma irradiation. The samples were exposed to 5.81×10^7 roentgens, equivalent to an absorbed dose of 5.47×10^9 ergs per gram of polymer.

Viscosity Measurements

Viscosities of the polymer samples were measured in benzene solutions at $30°C$ with Ubbelohde-type dilution viscometers having running times of about 170 sec for benzene. Kinetic energy and shear corrections were not made. Intrinsic viscosities were determined by the usual extrapolation of η_{sp}/c versus c plots. Number-average molecular weights, $\bar{M}_n$, were calculated from the relationship (15)

$$[\eta] = 1.97 \times 10^{-4} \bar{M}_n^{0.72}.$$

Procedure

The same general procedure as that described in our previous reports was used in this work. Films of polystyrene in flat, rectangular, quartz or Pyrex dishes of about 50-cm^2 area were formed by the slow evaporation of methylene chloride or tetrahydrofuran solutions containing 0.1 g of the polymer. These films were approximately 20μ thick. Volatile materials were almost completely eliminated by heating the dish containing the film in the irradiation cell at $120°C$ for at least 16 to 24 hours with continuous pumping at 10^{-5} torr.

Exposures in the absence of air were made at 10^{-5} torr at the desired temperature ($25°$, $80°$, or $120°C$) with the cell cut off from the spectrometer inlet system. The cell was then heated 4 hours at $120°C$ and the volatiles thus evolved expanded into the mass spectrometer for analysis. The same film could be cooled and re-exposed and the batchwise collection of products repeated. At the conclusion of a series of exposures with a given film, the cell was opened, the ultraviolet spectrum of the residual film was determined, and the film was taken up in benzene for the measurement of intrinsic viscosity. Exposures in air or in the presence of a known pressure of oxygen were carried out in an analogous fashion.

This procedure proved to be quite adequate for the determination of viscosity and ultraviolet spectral changes. It was also useful for the identification of the volatile products, as well as for a rough estimation of the quantum yields of these products. Reproducible quantitative determinations of the volatile products from polystyrene photolyses could not be obtained in this way, however, and it was necessary to modify the procedure. Since literature data on the reproducibility of mass spectral results in the polymer degradation field are limited (leading references are given by Wall (16)), the method used in this investigation will be given in some detail. It is probable that polystyrene represents an extreme case, since it is one of the most radiation-stable polymers and relatively large doses are required to produce a sufficient quantity of volatiles for analysis. Appropriate modifications of temperatures and times would be necessary when the method is used with other materials.

Rigorous cleaning of the dishes and the irradiation cell is absolutely essential. The dishes were cleaned with hot chromic acid, followed by water rinses. The possibility of surface catalysis of the polymer decomposition was not explored, but an effort was made to ensure identical surfaces in the glass dishes. Care must be taken to prevent adsorption

of atmospheric contaminants at the surface of the dishes after cleaning, since this will not only affect the adherence of the film to the dish but may well result in changes in the surface layer of the polymer film after it has been formed. The quartz irradiation cell was cleaned by repeated washings with a mild detergent and with water. Baking at 500°C for 24 hours resulted in complete outgassing of the cell.

It is necessary that each of the polymer films be formed under the same conditions. This was accomplished by allowing the polymer solutions to evaporate in the presence of each other in a semi-enclosed space. The same batch of solvent was used for all films.

Two such films in Pyrex dishes (which absorb 2537A radiation) were placed back-to-back in the irradiation cell and the entire assembly evacuated to 10^{-5} Torr and heated at 120°C for at least 62 hours, until no volatiles (only benzene was observed once methylene chloride was eliminated) could be detected in the mass spectrometer. Temperatures within the cell were continuously monitored by an iron-constantan thermocouple placed between the dishes. Once a run was begun, the cell was not allowed to cool below the temperature at which the irradiation was carried out. After the preliminary heating period, the cell was closed off from the spectrometer, and irradiation of one film was carried out for the desired time. The cell was again heated at 120°C for a suitable length of time, on the order of 48 hours. Finally, the accumulated gases were expanded into the mass spectrometer for analysis. An additional heating period at 120°C was used to ensure complete removal of volatiles between exposures. Irradiation of the second film was carried out in exactly the same manner as for the first film. This procedure of alternating exposures of the two films was repeated as often as required for one run.

RESULTS AND DISCUSSION

Molecular Weight Changes

As in our earlier work, molecular weight changes have been assessed on the basis of measurements of the viscosity of dilute solutions of the degraded polymer. The results are therefore subject to the restrictions of the method, since crosslinking was visually observed in all of our vacuum exposures as well as in the longer exposures in air.

Quantum yields were evaluated on the assumption that wherever apparent scission occurred it was a random process and that a "most probable" molecular weight distribution existed before and after degradation. The evaluations were made from plots of the number of scissions against the number of quanta absorbed per gram of polymer, i.e., $\left([\eta_o]/[\eta]\right)^{1/a} - 1$ versus $I_a t$, where a is the exponent of the Mark-Houwink equation and $[\eta_o]$ and $[\eta]$ are the intrinsic viscosities of the polymer before and after degradation. Quantum yields for scission are given by

$$\phi = (A/\bar{M}_{n_o})\left[\left([\eta_o]/[\eta]\right)^{1/a} - 1\right]/I_a t$$

where A is Avogadro's number and $\bar{M}_{n_o}$ is the initial number-average molecular weight of the polymer.

The results from exposures of polystyrene films to 2537A radiation are summarized in Fig. 2. At 25° and 120°C in air, these data lead to apparent initial quantum yields for random scission of 9×10^{-5} and 7×10^{-4} scissions per quantum absorbed, respectively. These quantum yields are only indicative of the different rates at the two temperatures, since benzene-insoluble material was evident at doses as low as 2×10^{21} quanta per gram at 120°C and at somewhat higher doses at room temperature. If the overall effect of crosslinking is to increase viscosity, then the true quantum yields for scission are probably higher than those given.
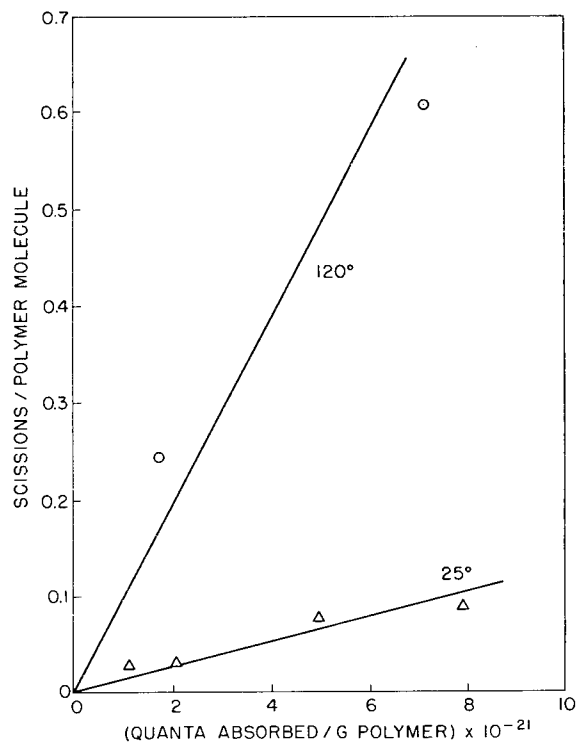
Fig. 2 - Apparent scissions occurring as
a function of irradiation in air

In the absence of air, ultraviolet irradiation of polystyrene films at 25°, 80°, and
120°C almost immediately results in the formation of benzene-insoluble material. For
a given dose, the proportion of insoluble polymer increases with irradiation temperature.
At the same time, the intrinsic viscosities of the soluble portions of the irradiated film
also increase, as shown in Fig. 3. The overall effect is therefore one of increasing cross-
linking as the irradiation temperature is increased through the range of 25° to 120°C.
This qualitative observation is seemingly at variance with that of Burlant and co-workers
(17) for polystyrene under gamma radiation. They reported the G-value for crosslinking
to be constant over the range -196° to 65°C and to decrease as the temperature was
increased from 98° to 130°C. Pravednikov and co-workers (18) found that additional
crosslinks formed when polystyrene gamma-irradiated at 25° was warmed to 95° but that
the degree of crosslinking was reduced if the irradiated samples were heated to 140°C.
Significantly, glass-transition points for polystyrene are about 80° to 100°C; above these
temperatures, chain mobility is greatly increased, and correspondingly, the ease of
crosslinking is increased. At the same time, it would be expected that the ease of dis-
proportionation, which competes with crosslinking, would also increase with temperature.
Thus, our results with ultraviolet irradiation agree with those with ionizing radiation for
this polymer. Similar findings in reference to the glass-transition temperature have been
reported for polyethylene under gamma irradiation (19) and for poly(ethyl acrylate) under
ultraviolet irradiation (20).

Oxygen apparently acts to prevent crosslinking by scavenging radicals along the
polymer chain. Such scavenging would not affect the scissioning process once a chain
break had occurred. Inhibition of crosslinking by oxygen during gamma-irradiation has
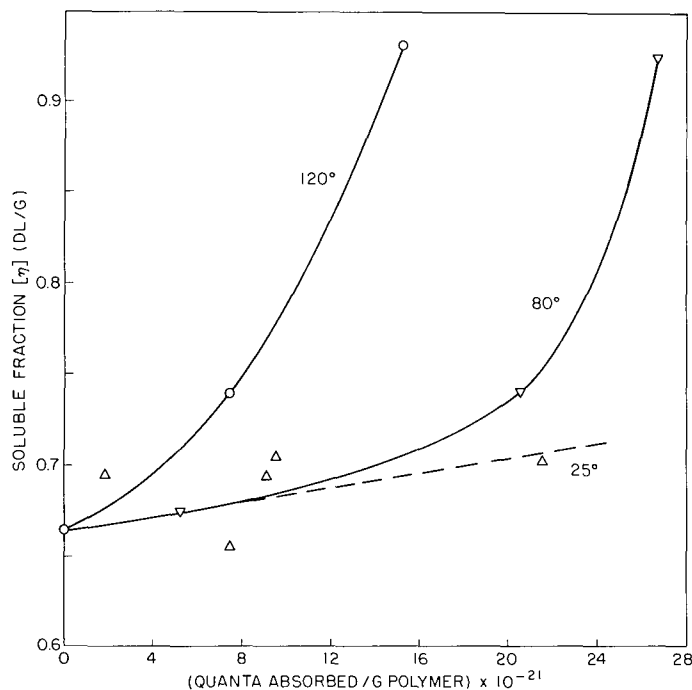been observed for many polymers, such as polyethylene (21).

Fig. 3 - Changes in the intrinsic viscosity of the
soluble fraction of polystyrene irradiated in vacuum

Comparative quantum yields for random scission for polystyrene and other polymers
having well-defined structures are given in Table 1. Analogous data for the radiolysis of
many of these polymers have also been reported (24). Those polymers having tertiary
hydrogen atoms in the backbone structure generally became crosslinked under any con-
ditions. Gel formation is fairly rapid in vacuum with polystyrene and poly(methyl acrylate);
and changes in the slope of the viscosity-dose curves for poly(methyl vinyl ketone) indi-
cate that with this polymer, also, crosslinking is taking place. Crosslinking was not
observed in polymers without tertiary hydrogen atoms in the backbone. The data in
Table 1 also indicate that the apparent stability of a tertiary-hydrogen-containing polymer
exceeds that of its methyl homolog. The order of stability in regard to major chromo-
phores is qualitatively $C_6H_5 \gg COOCH_3 > COCH_3$.

Table 1
Quantum Yields for Random Scission at Room Temperature

Polymer	Environment	$\phi_s \times 10^4$ (Scissions/quantum absorbed)	Reference
Polystyrene	Air	0.9	This report
Poly(α-methylstyrene)	Vacuum	10	1
Poly(methyl acrylate)	Air	130	5
Poly(methyl methacrylate)	Air	200	4
	Vacuum	300	4
Poly(methyl vinyl ketone)	Vacuum	200	22
Poly(methyl isopropenyl ketone)	Air	2200	23

Spectral Changes

Irradiation of polystyrene films in vacuum gives rise to a small general increase in absorption throughout the near-ultraviolet region of the spectrum. For example, at 80°C the transmittance of a typical film at 300 mμ changed from 0.94 prior to irradiation to 0.77 after absorption of 28×10^{21} quanta per gram. The rate at which these changes took place increased with increasing temperature, but the appearance of band structure at any temperature was not observed.

The changes in the absorption spectrum of a polystyrene film irradiated in air present a more interesting picture. As in the vacuum exposures, there is an overall increase in absorption in the near-ultraviolet region, but this increase occurs at a much faster rate in air than in vacuum. After the absorption of 7×10^{21} quanta per gram in air, a typical film will have a transmittance of 0.27 at 300 mμ.

In addition to the general increase in absorption, two bands in the form of weak shoulders at 282 and 340 mμ were observed in the spectra of films irradiated in air at room temperature.* After storage of the film for 72 hours in the dark, its absorption spectrum was unchanged. Other workers (8,9,12) have observed an increase in absorption at 340 mμ during storage at room temperature following irradiation of polystyrene at 60°C in air with a 3130A source. They also noted that this post-effect was removed by a brief re-exposure to the ultraviolet radiation. Since we have not observed the post-effect, we can only speculate that its origin lies in differences in composition in the two samples of polystyrene or in differences between the radiation sources. If the post-effect were due to a consumable impurity or structural anomaly present in both films, it is possible that in our experiments this impurity had been consumed during the irradiation. It is also possible that an intensity effect may be operating, since the absorption coefficient of polystyrene at 3130A is quite small, whereas all the incident 2537A radiation was absorbed by the films used in our work.

In the spectrum of styrene monomer, bands appear at 282 and 292 mμ. Since no shoulder in the spectrum appeared at 292 mμ, it seems unlikely that the 282-mμ shoulder is due to styrene monomer. Furthermore, when a sample of the irradiated material was dissolved in methylene chloride and reprecipitated with methanol, it was found that the 282-mμ shoulder was retained by the polymer, while the 340-mμ shoulder appeared in the filtrate. It is possible that the 282-mμ absorption is due to ketonic or aldehydic groups in the polymer chain, since such groups have been shown by infrared spectroscopy to be formed during the photo-oxidation of polystyrene. The source of the 340-mμ absorption is evidently a relatively small molecule or very short polymer fragment and may well be a compound of the type suggested by the earlier investigators (8,9).

It has been shown (25) that fast-electron irradiation of polystyrene in the absence of air produces changes in the infrared spectrum of the polymer, which can be ascribed to the formation of conjugated double bonds along the polymer backbone. Analogous changes may occur during ultraviolet irradiation in vacuum, and this would account for the differences in the ultraviolet spectra of our samples irradiated in air and in vacuum. Conjugated double bond formation should result in more than one structure, with a consequent smearing of several bands in the near-ultraviolet region. Similar double bond formation may also occur in air, but superimposed on the resulting spectra will be specific absorption due to oxygenated groups, which in turn may be the reason for the relatively high rate of increase in absorption during air irradiation.

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*Films irradiated at 120°C in air showed the 282-mμ shoulder at low doses; but during subsequent exposures, this absorption was overridden by general absorption increases. The 340-mμ shoulder was not observed in the 120°C exposures.

Volatile Products

As indicated in the Experimental Method section, quantitative reproducibility in the analysis of the volatile products was difficult to achieve. Qualitatively, the same products were always formed in the photolysis of films obtained from one batch of polymer. Even though every effort was made to make polystyrene samples PS-1 and PS-2 alike in all respects except molecular weight, differences between the samples can be seen in the volatile products. Most of the results reported here were obtained with films from polystyrene batch PS-2; the products were primarily hydrogen, carbon monoxide, carbon dioxide, methane, acetylene, benzene, and styrene. Multiple exposures using the "backto-back" technique were carried out with PS-1 films; the same products were formed, with one exception: ethylene, but no acetylene, was observed. Other oxygenated compounds were not detected among the volatile photolysis products from either of the polymer samples irradiated in vacuum.

One qualitative run with PS-2 under gamma irradiation at about 25°C showed the volatile products to consist primarily of hydrogen with traces of carbon dioxide and acetylene; carbon monoxide, methane, benzene, and styrene were not observed. In most radiolyses of polystyrene, hydrogen has been the only significant product (17).

Although the absolute quantum yields of the individual products or even the total gas yields from films of PS-2 did not correlate well with the absorbed dose of radiation, some useful information, both positive and negative, can be obtained by comparing the yields of products relative to each other. In three instances, a reasonable constancy in quantum yield ratios was found under a wide variety of conditions. These ratios were determined from the slopes of the curves in Figs. 4, 5, and 6 and are given in Table 2. Thus, some correlation in pairs of products can be obtained involving five of the seven compounds detected among the volatiles from the PS-2 polymer.
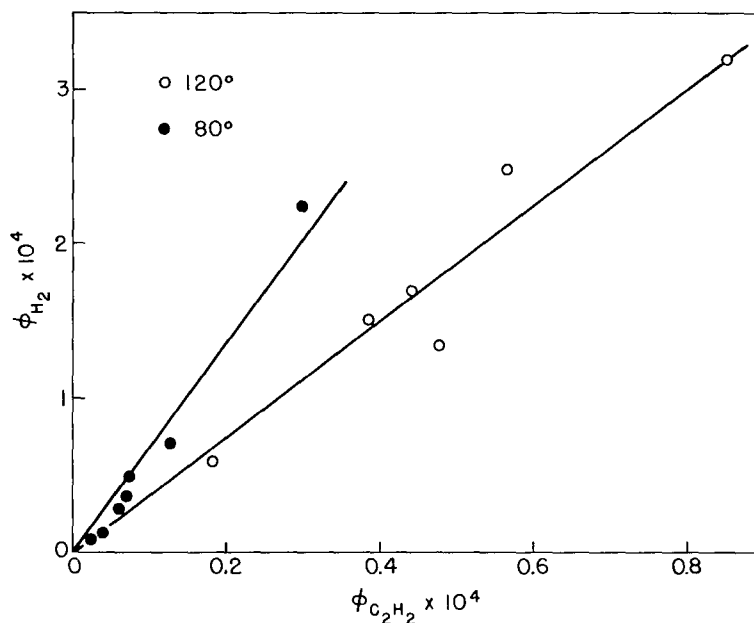

Fig. 4 - Relationship between hydrogen and acetylene
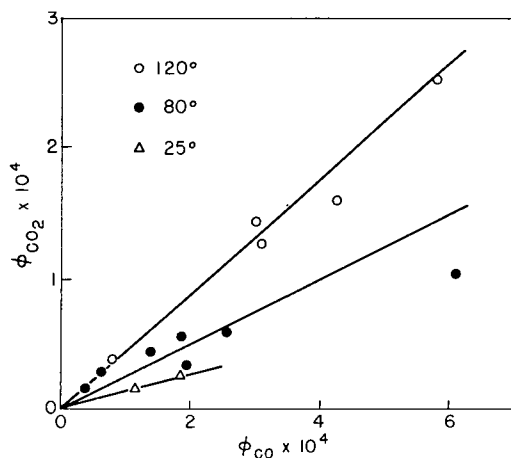formed during irradiation of PS-2

Fig. 5 - Relationship between carbon dioxide and carbon monoxide formed during irradiation of PS-2
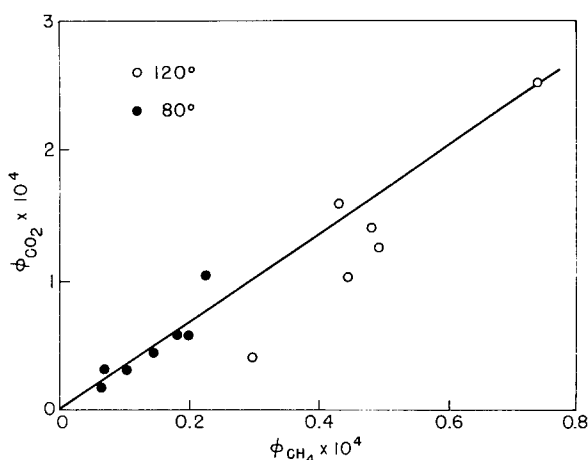

Fig. 6 - Relationship between carbon dioxide and methane formed during irradiation of PS-2

Table 2
Quantum Yield Ratios for Selected Volatile
Products From Irradiated Polystyrene (PS-2)

Irradiation Temperature (°C)	H_2/C_2H_2	CO/CO_2	CO_2/CH_4
25	–	7.5	–
80	7	4	3.3
120	3.7	2.4	3.3

The remaining data, for which little or no interrelationship can be determined, are collected in Table 3. For a given exposure, the second column gives the incremental absorbed dose, followed in parentheses by the total absorbed dose received prior to that exposure. The corresponding quantum yield for hydrogen formation is given in the third column. Subsequent columns contain certain calculated quantum yield ratios for the products formed. Should the absolute amount of any specific product be desired, it can be calculated from the ratio of that product to hydrogen and the absolute hydrogen quantum yield.

It is apparent that the widest deviations in Table 3 involve benzene and styrene, the two major products not included in Table 2. Evidently, these compounds are not formed entirely as a consequence of the photolysis of the polymer. Both benzene and styrene would be expected to adhere strongly to the solid polymer during the preliminary degassing operation, and both were probably present in the crude sample. As indicated in the earlier polystyrene work (10), however, irradiation of the solid polymer appears to increase permeability, and as a result, such residual low-molecular-weight impurities would be more likely to be released from the film.

Temperature has a marked effect on the rate of evolution of the products from the films, although there may be a question concerning the effect of temperature on the photodegradation process itself. At room temperatures, many products, especially the higher-molecular-weight and more strongly adherent compounds, are only detectable in trace

Table 3
Product Yield Ratios in Polystyrene (PS-2) Photolysis

Temp. (°C)	$I_a t \times 10^{-21}$ quanta absorbed/gram of polymer	$\phi_{H_2} \times 10^4$ molecules/ quantum absorbed	$\dfrac{H_2}{CO}$	$\dfrac{H_2}{CO_2}$	$\dfrac{H_2}{C_6H_6}$	$\dfrac{H_2}{CH_4}$	$\dfrac{H_2}{C_6H_5CH=CH_2}$	$\dfrac{CO}{C_2H_2}$
120	2.14 (0)*	1.71	0.54	1.35	1.15	3.6	11.5	7.2
	2.15 (0)	1.54	0.50	1.08	0.25	3.2	9.7	7.8
	2.21 (0)	1.33	0.31	0.83	0.46	3.1	8.3	9.0
	4.1 (0)	2.49	0.43	0.99	0.60	3.4	31.	10.2
	7.5 (4.1)	3.20	1.0	3.1	2.2	7.3	128.	3.8
	15.2 (2.15)	0.59	0.74	1.48	0.94	2.0	39.	4.2
80	1.64 (0)	0.72	0.28	1.21	0.61	3.7	5.5	20.
	5.18 (0)	0.29	0.15	0.88	3.3	4.3	13.2	29.
	5.26 (0)	2.23	0.37	2.1	>100.	10.0	–	21.
	6.41 (5.18)	0.36	0.26	0.80	1.1	2.5	10.6	19.
	4.5 (11.6)	0.48	0.70	1.58	1.9	4.7	12.7	9.0
	20.6 (16.1)	0.11	0.28	0.65	1.5	1.8	5.0	8.7
25	1.26 (0)	3.55	4.0					1.
	3.91 (1.26)	2.00	1.0					2.3
	4.11 (5.17)	0.27	0.14	1.0				–
	14.3 (9.28)	0.94	0.8		12.			15.

*Figures in parentheses denote irradiation dose which preceded the incremental dose recorded in this column.

amounts at most. The quantum yield for hydrogen formation tended to be much higher at room temperatures than at 80°C, but at 120°C the average hydrogen yield was greater than that at 80°C. Except for the hydrogen case, the product yields generally increased with temperature, although no sudden increase in passing through the glass-transition temperature (about 100°C) was evident. It has been reported (17) that hydrogen diffuses quantitatively and essentially instantly from powdered gamma-irradiated polystyrene even at -196°C.

It is of interest to compare the results of exposures of polystyrene samples PS-1 and PS-2. Polystyrene PS-1 was used only at 120°C with the relatively refined procedure described in the Experimental Method section in which pairs of films were exposed in the same cell. The qualitative differences in the nature of the volatile products from the two polystyrenes have already been noted. In addition, for a given dose the total gas yields from PS-1 were greater than from PS-2. Since the irradiations were preceded by an 84-hour heating period, during which only a very small amount of benzene was evolved, the high gas yields do not seem to be due to the presence of thermolabile linkages. Moreover, in one run, the first 4-hour exposure was followed by a 128-hour heating period in which the quantities of products approximately doubled those formed during the exposure itself. Since the total products formed at this point did not represent an excessive initial surge (relative to later exposures of the same films) of material, it would appear that the sample is nearly free of highly photolabile linkages as well. Lengthy heating periods after subsequent exposures produced no measurable amounts of products.

The cumulative formation of some of these products is shown in Fig. 7. This represents the results from two back-to-back runs, i.e., two pairs of PS-1 films. The reproducibility within a given pair of films is indicated by the length of the vertical lines at each point on the curves. Between the two runs the reproducibility is good only for hydrogen, and the quantum yields for hydrogen for both PS-1 and PS-2 samples were approximately the same, about 10^{-4} molecules per quantum absorbed. There is, therefore, reason to believe that hydrogen is formed almost entirely by the photolysis of polystyrene itself, as distinct from non-polymer material or from polymer imperfections such as points of oxidation along the chain. The viscometric results do not allow a correlation between hydrogen formation and the number of scissions or crosslinks. Wall and Brown (26) observed that under gamma irradiation, polystyrene undergoes crosslinking more rapidly than can be accounted for by hydrogen formation and suggested that the benzene ring may be involved in the crosslinking process.

Carbon monoxide and carbon dioxide can be formed only by the photolysis of impurities or of imperfections in the films, since there was no spectacular release of these substances in the early stages of the irradiation as might be expected if they were present initially as adsorbed species. Approximately the same ratio between carbon monoxide and carbon dioxide exists in the products from both the PS-1 and PS-2 samples, although the carbon dioxide:methane ratio for the PS-1 samples is much smaller (1.3) than for the PS-2 samples (3.3). This suggests that, although the formation of carbon monoxide, carbon dioxide, and methane may be involved in the same photolytic event, they must also represent more than one impurity or imperfection. A likely explanation is that carbon monoxide and carbon dioxide arise from the photolysis of groups formed by oxidation along the polymer chain, while methane arises from chain ends which may themselves be partially oxidized. That polystyrene may be undergoing continuous oxidation in air is supported by the disparity between the two runs shown in Fig. 7, since the run giving the greatest amounts of carbon monoxide and carbon dioxide was made some months after the first run.

The remaining volatile products, styrene, benzene, and ethylene, were evolved continuously during both runs with PS-1 films. As with the PS-2 films, there seemed to be little relationship among these and the other photolysis products. The first pair of PS-1 films exposed showed a much greater disparity between members of the pair and greater
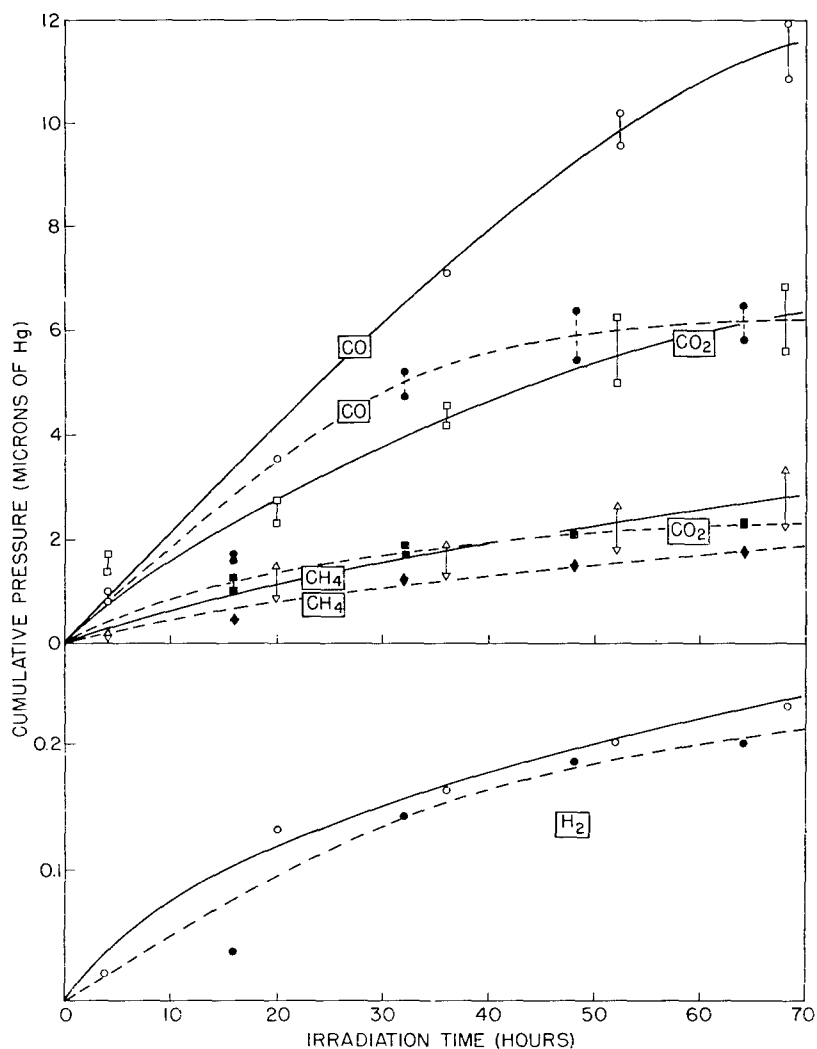
Fig. 7 - Comparison of product formation in two back-to-back
PS-1 runs at 120°C (vertical lines show spread between values
in a given run)

total yields of styrene, benzene, and ethylene. It is concluded that the bulk of these products must arise from impurities in the film rather than from photolysis of the polymer, even though it is reasonable to assume their formation at least in association with a main-chain scission.

The volatiles formed by irradiating polystyrene (PS-2) at 25°C in the presence of 20 torr of oxygen were investigated in a single run. After an absorbed dose of 10^{22} quanta per gram of polymer, there were evolved carbon dioxide, carbon monoxide, styrene, and benzene in quantum yields of 250, 100, 1.4, and 0.2×10^{-4} molecules per quantum absorbed, respectively. Water was also formed in relatively large quantities, but hydrogen, alcohols and other oxygenated products, and other hydrocarbons were absent. Hydrogen was probably consumed by reaction with oxygen. Acetylene, if formed, must have been completely oxidized, although, if such is the case, some products of oxidation of styrene should also have been encountered. No measure was made of the residual oxygen incorporated in the

polymer after irradiation under our conditions, but Achhammer and co-workers (10) have reported that at 118°C under 3130A radiation, stable oxygenated structures are readily formed in polystyrene by oxygen.

GENERAL CONSIDERATIONS

The picture of polystyrene photodegradation presented here is somewhat obscured by the very fact of the high photostability of the polymer. Even though more refined techniques and perhaps purer materials have been employed in comparison with those of other investigations, the conclusions are still qualitative and represent primarily confirmation and elaboration of those given earlier. Some 21 volatile compounds, 10 of which contain oxygen, have been reported (10) as photolysis products from polystyrene subjected to 3130A radiation at 120°C in vacuum. We have narrowed this plethora of products to seven compounds, including carbon monoxide and carbon dioxide, but six of these materials appear to have evolved from substances other than pure polystyrene. Thus, the study of polystyrene photolysis actually is a study of the photolysis of impurities and imperfections in polystyrene and their effect on its photodegradation.

During irradiation in vacuum, simultaneous scissioning of the main chain and crosslinking between chains takes place with the number of crosslinks exceeding the number of scissions. This is probably also the case in the air exposures, but with a reduction in crosslinking due to the scavenging of secondary- or tertiary-polymer free radicals by oxygen. Hydrogen seems to be the only volatile product which emanates from the photolysis of the pure polymer, and it is most likely associated with the crosslinking process.

Combined oxygen must play a leading role in the photodegradation of polystyrene. This oxygen must be present in some relatively stable form, rather than as, for example, readily ruptured peroxide links in the polymer backbone. Oxygen-containing groups may be located at the site of a main-chain scission and thus the carbon monoxide and carbon dioxide formed may be associated with the scissioning process. Some evidence for this was found in earlier work on poly(α-methylstyrene) (1). The further association of methane with the carbon monoxide and carbon dioxide is a complicating factor, but its variation between batches suggests that methane must form only from specific oxygen-containing groups, possibly at the ends of polymer chains.

Although some depolymerization of polystyrene occurs during thermal degradation, this must be at best a very minor process in photodegradation at 120°C and below. Both styrene and benzene were evolved during irradiation, but in such a fashion as to indicate their presence primarily as impurities. It is tempting to write reactions which lead to the formation of benzene, because account may then be made for the spectral changes as being a result of conjugated unsaturation along the main chain. Sufficient speculation has been made by others (8,9) regarding oxygenated groups as the responsible chromophores.

The formation of acetylene in one batch and ethylene in another batch of nearly identical polystyrene points up once again the fact that the most minor photolytic features of a sample loom large next to the actual degradation itself. There is at present no adequate explanation for this difference in behavior of the two samples, except to again ascribe the presence of acetylene or ethylene to impurities.

REFERENCES

1. Stokes, S., and Fox, R.B., "Photodegradation of High Polymers, Part II - Vacuum Photolysis of Poly-α-Methylstyrene," NRL Report 5591, Feb. 1961; J. Polymer Sci. 56:507 (1962)

2. Fox, R.B., and Price, T.R., "Photodegradation of High Polymers in Solution, Part I - Solvent Effects in the Photolysis of Poly(α-Methylstyrene)," NRL Report 6120, Aug. 1964; J. Polymer Sci., in press.

3. Fox, R.B., and Price, T.R., "Photodegradation of High Polymers in Solution, Part 2 - Solvent Effects in the Photolysis of Polystyrene" NRL Report in preparation

4. Fox, R.B., Isaacs, L.G., Stokes, S., and Daasch, L.W., "Photodegradation of High Polymers, Part III - Photolysis of Poly(Methyl Methacrylate) in Vacuum and in Air," NRL Report 5720, Dec. 1961; J. Polymer Sci. A1:1079 (1963)

5. Fox, R.B., Isaacs, L.G., Stokes, S., and Kagarise, R.E., "Photodegradation of High Polymers, Part IV - Photolysis of Poly(Methyl Acrylate) in Vacuum and in Air," NRL Report 5894, Feb. 1963; J. Polymer Sci. A2:2085 (1964)

6. Jellinek, H.H.G., Pure and Appl. Chem. 4:419 (1962)

7. Grassie, N., "Chemistry of High Polymer Degradation Processes," New York:Interscience Publishers (1956)

8. Tryon, M., and Wall, L.A., J. Phys. Chem. 62:697 (1958)

9. Wall, L.A., Harvey, M.R., and Tryon, M., J. Phys. Chem. 60:1306 (1956)

10. Achhammer, B.G., Reiney, M.J., Wall, L.A., and Reinhart, F.W., J. Polymer Sci. 8:555 (1952)

11. Achhammer, B.G., Reiney, M.J., and Reinhart, F.W., J. Res. Nat. Bur. Std. 47:116 (1951)

12. Reiney, M.J., Tryon, M., and Achhammer, B.G., J. Res. Nat. Bur. Std. 51:155 (1953)

13. McDowell, M.V., Isaacs, L.G., Fox, R.B., and Saalfeld, F.E., "An Inexpensive Portable Radiation Source Shield" in Report of NRL Progress, No. 37, Nov. 1963

14. Hatchard, C.G., and Parker, C.A., Proc. Roy. Soc. (London), A235:518 (1956)

15. Meyerhoff, G., Z. physik. Chem. 4:336 (1955)

16. Wall, L.A., in "Analytical Chemistry of Polymers, Part II - Analysis of Molecular Structure and Chemical Groups," G.M. Kline, editor, New York:Interscience Publishers (1962)

17. Burlant, W., Neerman, J., and Serment, V., J. Polymer Sci. 58:491 (1962)

18. Pravednikov, A.N., Yin-Shen-Kan, and Medvedev, S.S., Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 29:192 (1958)

19. Williams, T.F., and Dole, M., J. Am. Chem. Soc. 81:2919 (1959)

20. Jacobs, H., and Steele, R., J. Appl. Polymer Sci. 3:245 (1960)

21. Matsuo, H., and Dole, M., J. Phys. Chem. 63:837 (1959)

22. Wissbrun, K.F., J. Am. Chem. Soc. 81:58 (1959)

23. Shultz, A.R., J. Polymer Sci. 47:267 (1960)

24. Chapiro, A., "Radiation Chemistry of Polymeric Systems," New York:Interscience Publishers (1962)

25. Slovokhotova, N.A., Iliecheva, Z.F., and Kargin, V.A., Vysokomol. Soedin. 3:191 (1961)

26. Wall, L.A., and Brown D.W., J. Phys. Chem. 61:129 (1957)

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
U.S. Naval Research Laboratory Washington, D.C. 20390	Unclassified
	2b. GROUP

3. REPORT TITLE

PHOTODEGRADATION OF HIGH POLYMERS, PART VI - PHOTOLYSIS OF POLYSTYRENE FILMS IN VACUUM AND IN AIR

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on one phase of the problem.

5. AUTHOR(S) *(Last name, first name, initial)*

Fox, R.B., Isaacs, L.G., Saalfeld, F.E., and McDowell, M.V.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
June 16, 1965	20	26

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
NRL Probs. C04-04 and C07-02	
b. PROJECT NO.	NRL Report 6284
RR 001-02-43-4801 and RR 001-01-	
c. 43-4804	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. AVAILABILITY/LIMITATION NOTICES

Unlimited availability - Available from CFSTI - $1.00

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Dept. of the Navy (Office of Naval Research)

13. ABSTRACT

    Thin films of polystyrene have been photolyzed by 2537A radiation in vacuum and in air at 25°, 80°, and 120°C. Random scission and crosslinking occur simultaneously, with oxygen acting to inhibit the latter process. In air, the apparent quantum yields for random scission, measured by viscosity changes, are 9×10^{-5} and 7×10^{-4} scissions per quantum absorbed at 25° and 120°C, respectively. Crosslinks exceed scissions in vacuum, and no reduction in viscosity is observed; the ratio of crosslinks to scissions increases with temperature in the 25° to 120°C range. During photolysis, hydrogen appears to be the major volatile product emanating from the polymer itself. Of the remaining volatile products, carbon monoxide, carbon dioxide, and methane probably arise from polymer imperfections; benzene and monomer are present as impurities rather than major photolysis products. Large variations in the product yields, which are very small on an absolute scale, and the detection of ethylene from one batch and acetylene from another emphasize the importance of small impurities and imperfections in the photolysis of a highly stable polymer such as polystyrene. Changes in the ultraviolet spectra during photolysis are compatible with the formation of conjugated double bonds along the main chain; in air, these changes are supplemented by oxidation which results in carbonyl formation along the chain and a relatively small fragment absorbing at about 340 mμ.

DD FORM 1 JAN 64 1473

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Polystyrene Scission Polymer degradation Irradiation Photodegradation Crosslinking Photolysis Ultraviolet radiation						

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